

DESCRIPTION

ULTRAVIOLET-CROSSLINKABLE POLYMER COMPOSITION

5

TECHNICAL FIELD

The present invention relates to a polymer composition having iodine and/or bromine which is crosslinkable by irradiation with ultraviolet rays.

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BACKGROUND ART

For crosslinking a fluorine-containing polymer, particularly a fluorine-containing elastomer, usual crosslinking methods are polyamine vulcanization, polyol vulcanization and organic peroxide vulcanization. In any of those methods, a high temperature is
15 necessary in order to obtain a crosslinked article and therefore an application thereof is limited.

Particularly in case of a method of crosslinking a fluorine-containing elastomer having iodine or bromine, generally a method of crosslinking with an organic peroxide is employed. However the
20 crosslinking needs to be carried out at high temperature and in case of usual molding, a crosslinking reaction does not proceed in the neighborhood of an interface with oxygen and staining of a metal die arises. Thus there is a problem with processability.

JP-B-5-63482, etc. describe crosslinking methods other than
25 the method of crosslinking by using heat energy, namely methods of crosslinking by using radiation, etc. Such methods require expensive facilities and are not carried out easily and therefore application thereof

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is limited to only particular fields.

For example, in crosslinking of a fluorine-containing polymer, ionizing radiation, etc. have been adopted practically for crosslinking of a tetrafluoroethylene-ethylene copolymer (ETFE), polyvinylidene fluoride (PVdF), and the like, but only in the field of electric cables. As for perfluoropolymers, it is assumed that crosslinking thereof is still difficult.

On the other hand, urethane rubber and silicone rubber are on the market and are widely used because crosslinking need not be carried out at high temperature and can be carried out at room temperature. However the urethane rubber has a problem with heat resistance and water resistance, and the silicone rubber has a problem with chemical resistance and oil resistance.

As mentioned above, there have been no fluorine-containing polymer compositions which could be cured at room temperature while maintaining excellent properties of the fluorine-containing polymer.

An object of the present invention is to provide a crosslinkable composition comprising a polymer containing iodine and/or bromine in a specific amount, particularly an ultraviolet-crosslinkable fluorine-containing polymer, and also to provide a crosslinked article obtained from the composition.

DISCLOSURE OF INVENTION

The present invention relates to an ultraviolet-crosslinkable polymer composition which comprises a polymer containing 0.001 to 10 % by weight of iodine and/or bromine, a photoinitiator as a crosslinking agent and a polyfunctional unsaturated compound as a

crosslinking aid.

When the polymer is a fluorine-containing polymer, particularly a fluorine-containing elastomer, an excellent effect is exhibited.

5 Hitherto in crosslinking with ultraviolet rays, usually an acryl group is activated by irradiation of ultraviolet rays to become a crosslinking point. However in the present invention, iodine or bromine contained in the polymer is a crosslinking point. Such a crosslinking system has not been known and is a novel one.

BEST MODE FOR CARRYING OUT THE INVENTION

In the present invention the polymer having iodine and/or bromine may be a resin or an elastomer.

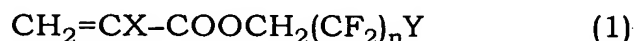
10 For introducing iodine or bromine into the polymer, various known methods can be used. For example, there are (1) a method of copolymerizing a monomer having iodine and/or bromine (hereinafter referred to as "Introducing Method 1". JP-A-8-53595, JP-B-5-63482, JP-A-4-288305, JP-B-53-4115, etc.); (2) a method of using an iodine or bromine compound as a polymerization initiator or a chain transfer agent (hereinafter referred to as "Introducing Method 2". JP-A-63-23907, JP-B-6-11773, JP-B-1-16844, JP-B-63-41928, JP-B-5-406, JP-A-62-36407, etc.), and the like. The introducing method is not limited to them.

25 First, a resin as a basic component is explained below. Either of a non-fluorine-containing resin and a fluorine-containing resin may be used as a resin.

Examples of the non-fluorine-containing resin are, for

instance, homopolymers or copolymers of poly(meth)acrylic acid esters such as polymethyl methacrylate and polyethyl acrylate. Examples of the monomer to be used are methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, and the like. Examples of the
5 comonomer are, for instance, ethylene, propylene, vinyl chloride, vinylidene chloride, acrylonitrile, vinyl esters such as vinyl acetate, vinyl ethers such as ethyl vinyl ether, vinyl monomers such as styrene, and the like.

Examples of the fluorine-containing resin are homopolymers
10 or copolymers of fluorine-containing (meth)acrylic acid esters represented by the formula (1):



15 wherein X is H, F or CH₃, n is an integer of from 1 to 8, Y is H or F. Examples of the comonomer are the above-mentioned (meth)acrylic acid esters and/or vinyl monomers.

Also there are polytetrafluoroethylene, polyvinylidene fluoride, ethylene-tetrafluoroethylene copolymer, ethylene-
20 chlorotrifluoroethylene copolymer, tetrafluoroethylene-hexafluoropropylene copolymer, tetrafluoroethylene-perfluoro(alkyl vinyl ether) copolymer, and the like.

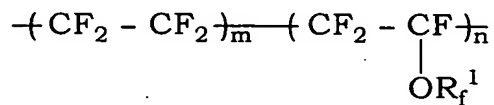
While the elastomer to be used in the present invention may be a non-fluorine-containing elastomer, particularly a fluorine-
25 containing elastomer which has been unable to be crosslinked with ultraviolet rays can be used preferably. Examples of the fluorine-containing elastomer are, for instance, vinylidene fluoride copolymers

such as vinylidene fluoride-hexafluoropropylene copolymer, vinylidene fluoride-tetrafluoroethylene-hexafluoropropylene copolymer and vinylidene fluoride-chlorotrifluoroethylene copolymer; tetrafluoroethylene-propylene copolymer and ethylene-hexafluoropropylene copolymer; fluoro(alkyl vinyl ether) (encompassing those having plural ether bonds)-olefin copolymers such as vinylidene fluoride-tetrafluoroethylene-perfluoro(alkyl vinyl ether) copolymer and tetrafluoroethylene-perfluoro(alkyl vinyl ether) copolymer; alkyl vinyl ether-chlorotrifluoroethylene copolymer, and the like.

Also other monomer component copolymerizable thereto may be copolymerized. Examples thereof are vinyl chloride, vinylidene chloride, acrylonitrile, vinyl esters such as vinyl acetate, vinyl ethers such as ethyl vinyl ether, styrene, and the like.

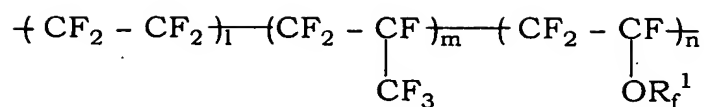
In the present invention the fluorine-containing elastomer may be the above-mentioned fluorine-containing elastomers and in addition, those having, as an elastomer chain, a perfluoro elastomer chain represented by the following formula (2) or (3) or a non-perfluoro elastomer chain represented by the formula (4), (5), (6) or (7).

A copolymer elastomer chain represented by the formula (2):



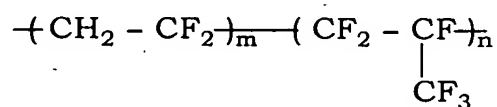
wherein m is from 95 to 50, n is from 5 to 50, R_f^1 is a perfluoroalkyl group having 1 to 8 carbon atoms,

A terpolymer elastomer chain represented by the formula (3):



wherein l is from 95 to 35, m is from 0 to 30, n is from 5 to 35, R_f^1 is a
5 perfluoroalkyl group having 1 to 8 carbon atoms,

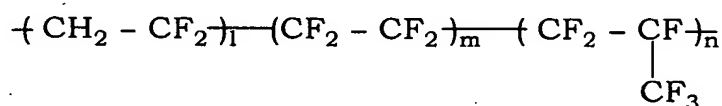
A copolymer elastomer chain represented by the formula (4):



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wherein m is from 85 to 60, n is from 15 to 40,

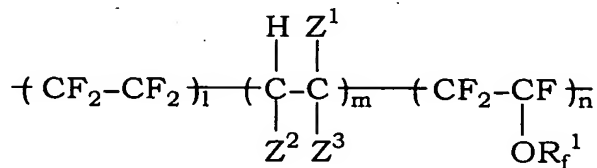
A terpolymer elastomer chain represented by the formula (5):



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wherein l is from 85 to 20, m is from 0 to 40, n is from 15 to 40,

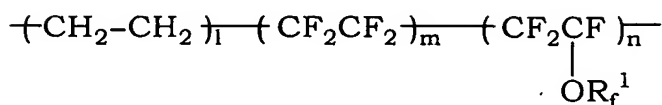
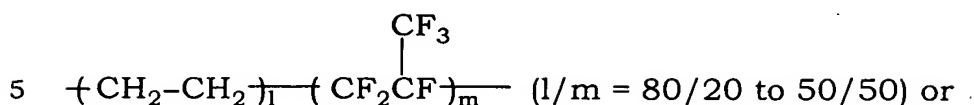
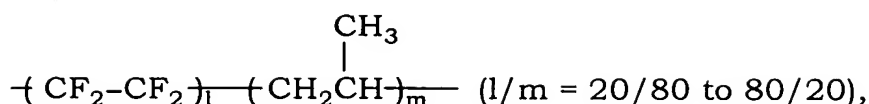
A terpolymer elastomer chain represented by the formula (6):



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wherein l is from 95 to 45, m is from 0 to 10, n is from 5 to 45, Z^1 , Z^2 and
25 Z^3 are fluorine atom or hydrogen atom independently, R_f^1 is a
perfluoroalkyl group having 1 to 8 carbon atoms, and

A non-perfluoro elastomer chain represented by the formula (7):



- 10 (l is from 1 to 80, m is from 0 to 80, n is from 10 to 50, R_f¹ is as defined above).

Further there may be used a fluorine-containing multi-segment polymer prepared by block-copolymerizing the above-mentioned elastomer as an elastomer segment with a fluorine-
15 containing resin as a hard segment.

Then the monomer for introducing iodine and/or bromine is explained below.

Examples of the monomer having iodine and/or bromine which can be used in Introducing Method 1 are monomers described in
20 the above-mentioned JP-A-8-53595. Examples thereof are, for instance, CH₂=CHCH₂OCOCF₂CH₂I, CH₂=CHCOOCH₂CH₂(CF₂)₄I, CH₂=CHCOOCH₂CH₂I, CH₂=CHCH₂OCH₂CH₂(CF₂)₄I, CH₂=CHCH₂OCH₂CH₂I, CH₂=CHCH₂OCOCF₂CH₂Br, CH₂=CHCOOCH₂CH₂(CF₂)₄Br, CH₂=CHCOOCH₂CH₂Br,
25 CH₂=CHCH₂OCH₂CH₂(CF₂)₄Br, CH₂=CHCH₂OCH₂CH₂Br, and the like. It is preferable that those iodine- and/or bromine-containing monomers are used for the non-fluorine-containing polymers from the viewpoint of

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copolymerizability.

Also there are monomers described in the above-mentioned JP-B-5-63482, JP-A-4-288305, JP-B-53-4115, etc. Examples thereof are, for instance, $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CH}_2\text{I}$,
5 $\text{CF}_2=\text{CFOCF}_2(\text{CF}_3)\text{CFOCF}_2\text{CF}_2\text{CH}_2\text{I}$, $\text{CF}_2=\text{CFI}$, $\text{CF}_2=\text{CHBr}$,
 $\text{CH}_2=\text{CHCF}_2\text{CF}_2\text{Br}$, $\text{CF}_2=\text{CFOCF}(\text{CF}_3)\text{CF}_2\text{OCF}_2\text{Br}$, and the like. It is preferable that those iodine- and/or bromine-containing monomers are used for the fluorine-containing polymers from the viewpoint of copolymerizability.

10 Polymerization methods which can be used for this introducing method are known methods such as emulsion polymerization, suspension polymerization, solution polymerization, and the like.

The monomer is copolymerized in such an amount that
15 iodine and/or bromine are contained in the obtained polymer in an amount of from 0.001 to 10 % by weight, preferably from 0.05 to 7 % by weight.

Introducing Method 2 is a method of introducing iodine and/or bromine into an end of the polymer by using iodine and/or
20 bromine or a compound having iodine and/or bromine as a polymerization initiator or a chain transfer agent.

Examples of such a polymerization initiator are, for instance, those described in the above-mentioned JP-A-63-23907. Concretely there are, for example, $(\text{ICF}_2\text{COO})_2$, and the like.

25 Examples of such a chain transfer agent are, for instance, those described in the above-mentioned JP-B-6-11773, JP-B-1-16844, JP-B-63-41928, JP-B-5-406, JP-A-62-36407, etc. Concretely there are,

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for example, $\text{I}(\text{CF}_2)_4\text{I}$, CH_2I_2 , $(\text{ICF}_2\text{CF}_2)_2\text{C}_6\text{F}_4$, CF_2Br_2 , $\text{BrCH}_2\text{CH}_2\text{I}$, and the like. It is preferable that those iodine- and/or bromine-containing monomers are used for the fluorine-containing polymers from the viewpoint of chain transfer reaction.

5 Particularly from the viewpoint of easiness of crosslinking reaction, iodine-containing monomers are preferable.

Examples of a polymerization method which can be used for those introducing methods are known methods such as emulsion polymerization, suspension polymerization and solution polymerization.

10 The polymers must contain iodine or bromine (a total amount thereof when the both are contained) in an amount of from 0.001 to 10 % by weight. When the amount is less than 0.001 % by weight, crosslinking cannot be carried out sufficiently, and when the amount is more than 10 % by weight, properties of the polymer such as heat
15 resistance are lowered. The preferred content thereof is from 0.05 to 7 % by weight.

From the viewpoint of high crosslinking reactivity, it is preferable that the polymers mainly contain iodine rather than bromine.

In the present invention, the iodine- and/or bromine-
20 containing polymers may be used alone or in a mixture of two or more thereof. The polymers may be blended to other polymer which does not contain iodine (bromine). Examples of the other non-iodine (non-bromine)-containing polymer which may be blended are, for instance, ultraviolet-crosslinkable polymers, such as epoxy acrylate, urethane
25 acrylate, polyester acrylate and polyether acrylate.

The ultraviolet-crosslinkable polymer composition of the present invention comprises the above-mentioned iodine- and/or

bromine-containing polymer, a photoinitiator and a polyfunctional unsaturated compound.

The photoinitiator to be used in the present invention acts as a crosslinking agent, and photoinitiators which have been known in ultraviolet crosslinking can be used. Examples thereof are acetophenone initiators such as chloroacetophenone, diethoxyacetophenone, α -aminoacetophenone, and hydroxyacetophenones, i.e. 2-hydroxy-2-methyl-1-phenylpropane-1-one, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropane-1-one and 1-hydroxycyclohexylphenylketone; benzoine initiators such as benzoine, benzoine ether and dimethylbenzyl ketal; benzophenone initiators such as benzophenone, benzoylbenzoic acid, hydroxybenzophenone, 4-phenylbenzophenone and acrylated benzophenone; thioxanthone initiators such as thioxanthone, 2-methylthioxanthone and 2,4-dimethylthioxanthone; α -acyloxime ester, acylphosphine oxide, benzyl, camphorquinone, 2-ethylanthraquinone, Michler's ketone, and the like.

An amount of the photoinitiator is usually from about 0.05 to about 10 parts by weight (hereinafter referred to as "part"), preferably from 1 to 5 parts based on 100 parts of the above-mentioned iodine- and/or bromine-containing polymer.

In case of benzophenone or thioxanthone initiators, a hydrogen donor may be added as a photoinitiating aid. Examples of the hydrogen donor are, for instance, aliphatic amines such as triethanolamine, methyldiethanolamine and triisopropanolamine; aromatic amines such as 4,4'-diethylaminophenone, 4-dimethylaminoethyl benzoate and 4-dimethylamino(n-butoxy)ethyl benzoate, and the like.

An amount of the hydrogen donor is usually from about 0.05 to about 10 parts, preferably from 0.5 to 5 parts based on 100 parts of the above-mentioned polymer.

The polyfunctional unsaturated compound to be used in the present invention acts as a crosslinking aid. The polyfunctional unsaturated compound is not limited and is effective as far as it has a reactivity against both of a polymer radical derived from iodine and/or bromine and generated by irradiation of ultraviolet rays and a radical derived from the photoinitiator.

Examples of the preferable polyfunctional unsaturated compound are, for instance, various diacrylates, trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate, triallyl isocyanurate (TAIC), triallyl cyanurate, triallyl trimellitate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, N,N'-m-phenylenebismaleimide, dipropargyl terephthalate, diallyl phthalate, tetraallyl terephthalamide, triallyl phosphate, and the like. Among them, those having three or more functional groups are particularly preferable from the viewpoint of easiness of crosslinking of the polymer.

An amount of the polyfunctional unsaturated compound is from about 0.05 to about 10 parts, preferably from 0.5 to 5 parts based on 100 parts of the above-mentioned polymer.

Also as the case demands, a filler, processing aid, antioxidant, age resister, antiozonant, ultraviolet ray absorber, and the like may be blended.

Examples of the filler are metal oxides such as magnesium oxide, calcium oxide, titanium oxide, silicon oxide and aluminum oxide,

metal hydroxides such as magnesium hydroxide, aluminum hydroxide and calcium hydroxide, carbonates such as magnesium carbonate, aluminum carbonate, calcium carbonate and barium carbonate, silicates such as magnesium silicate, calcium silicate, sodium silicate
5 and aluminum silicate, sulfates such as aluminum sulfate, calcium sulfate and barium sulfate, synthetic hydrotalcite, metal sulfides such as molybdenum disulfide, iron sulfide and copper sulfide, diatom earth, asbestos, lithopone (zinc sulfide/barium sulfate), graphite, carbon black, carbon fluoride, calcium fluoride, coke, fluorine-containing resin, and
10 the like.

Examples of the processing aid are higher fatty acids such as stearic acid, oleic acid, palmitic acid and lauric acid; higher fatty acid salts such as sodium stearate and zinc stearate; higher fatty acid amides such as stearic acid amide and oleic amide; higher fatty acid esters such
15 as ethyl oleate; higher fatty acid amines such as stearylamine and oleilamine; petroleum wax such as carnauba wax and ceresine wax; polyglycols such as ethylene glycol, glycerine and diethylene glycol; aliphatic hydrocarbons such as vaseline and paraffin; silicone oil; silicone polymer; low molecular weight polyethylene; phthalic acid
20 esters; phosphoric acid esters; rosin; (halogenated) dialkylamine; (halogenated) dialkylsulfone, surfactant; and the like.

Examples of the antioxidant, age resister and antiozonant are phenol compounds such as 2,5-di-t-amylhydroquinone, amine-ketone compounds such as 2,2,4-trimethyl-1,2-dihydroquinone, aromatic
25 binary amine compounds such as 4,4'-bis(α,α -dimethylbenzyl)diphenylamine, and the like.

Examples of the ultraviolet ray absorber are benzophenone

compounds such as 2,4-dihydroxybenzophenone, amine compounds
such as bis(2,2,6,6-tetramethyl-4-piperizyl)sebacate, benzotriazole
compounds such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, and
the like. An adding amount thereof differs depending on kind of
5 additives and should be an amount not impairing a crosslinking reaction
with ultraviolet rays.

The composition of the present invention can be prepared by
known mixing methods. When the polymer is a resin, the mixing may
be carried out at a temperature of not less than a melting point thereof
10 by using an internal mixer, segment extruder, two-screw extruder, or
the like. When the polymer is an elastomer and a molecular weight
thereof is high, kneading may be carried out with an internal mixer such
as an open roll or kneader mixer, and when the molecular weight thereof
is low, mixing may be carried out with a planetary mixer, portable mixer,
15 or the like. As far as the preparation is carried out in the room, there is
no serious problem, but it is desirable that the mixing is carried out
under the condition that no photo energy activating the photoinitiator is
irradiated. Also the mixing may be carried out in a solution by using a
good solvent.

20 In the present invention, suitable ultraviolet rays are those
having a wavelength of from 420 to 150 nm. Also those having a
wavelength range covering a maximum absorption wavelength of the
above-mentioned photoinitiator can be used.

The composition of the present invention can be subjected to
25 crosslinking with radiation and electron beams. The composition may
be crosslinked with radiation or electron beams and as the case
demands, in combination with ultraviolet rays. An irradiation time

varies depending on an intensity of ultraviolet rays, kind of photoinitiator, etc. When the intensity of the irradiation is about 165 mW/cm², the irradiation time of from about ten seconds to about five minutes is enough. The irradiation can be carried out at room
5 temperature.

The composition of the present invention is formed into a crosslinked article by crosslinking with ultraviolet rays. The crosslinked article can be used for various known applications. Particularly when a fluorine-containing polymer is used as a component
10 polymer, the crosslinked article can be used for various parts in automotive industry, airplane industry and semiconductor industry by making the use of its excellent heat resistance, oil resistance, amine resistance, chemical resistance, etc. Further when a fluorine-
15 containing elastomer is used, by utilizing its heat resistance, oil resistance and amine resistance, the crosslinked article can be used suitably for parts for oil sealing, for example, a hose, oil seal, etc. for engine oil of automotive, and also by utilizing its property of releasing less outgas, the crosslinked article can be used suitably for a gasket for a magnetic disc production apparatus, sealing materials for
20 semiconductor production apparatuses and lines, etc.

Also the composition of the present invention can be used as a coating material. Concretely by dissolving or dispersing the composition of the present invention in a solvent such as water or organic solvent, a coating material which can be crosslinked with
25 ultraviolet rays (further as the case demands, electron beams) is obtained.

The crosslinked article of the present invention can be

applied on the following molded articles, but the application is not limited to them.

Applications of molded articles:

Packing, O-ring, hose, other sealing material, diaphragm and
5 valve having amine resistance, oil resistance, chemical resistance, steam
resistance and weather resistance in transportation means such as
automotive, ship and airplane; similar packing, O-ring, sealing material,
diaphragm, valve, hose, roll and tube in chemical plant; similar packing,
O-ring, hose, sealing material, belt, diaphragm, valve, roll and tube in
10 foods plant and foods processing machine (including domestic
appliances); similar packing, O-ring, hose, sealing material, diaphragm,
valve and tube in nuclear plant; similar packing, O-ring, hose, sealing
material, diaphragm, valve, roll, tube, mandrel, cable, flexible joint, belt,
rubber plate and weatherstrip in general industrial parts; roll, roll blade
15 and belt for PPC copying machine, etc.

More concretely there are the following applications.

(i) Automotive applications

① For sealing

20 Crank shaft seal
Gear box seal
Power piston packing
Cylinder liner seal
Valve stem seal
Front pump seal for automatic transmission
25 Rear axle pinion seal
Gasket for universal joint
Pinion seal for speed meter

Bearing seal

Twin-carburetor tube

Diaphragm for sensor of carburetor

Hose for after burner

① For sealing

Joint seal for air duct

② For roll

Roll having trichlene resistance (for dyeing of fiber)

③ Other applications

Acid resistant hose (for concentrated sulfuric acid)

Packing for joint of tubes for gas chromatograph and pH
meter

Chlorine gas transfer hose

Rainwater drain hoses for benzene and toluene reservoir
tanks

Seal, tube, diaphragm and valve parts for analyzer and
physical and chemical appliances

(iii) Applications in industrial machinery

① For sealing

Seals for hydraulic and lubricating machine

Bearing seal

Seal for dry copying machine

Seals for window, etc. of dry cleaner

Seal for equipment for concentrating uranium hexafluoride

Seal (vacuum) valve for cyclotron

Seal for automatic packaging machine

② Other applications

Rolls, scraper, tube and valve parts for printing equipment

Rolls, scraper, tube and valve parts for coating equipment

Ink tube, roll and belt for printer

Belt and rolls for dry copying machine

Diaphragms for pumps for analyzing sulfurous acid gas and
chlorine gas in the air (environmental pollution-related
meters)

Rolls and belt for printer

Squeeze rolls for pickling

(iv) Airplane applications

Valve stem seal for jet engine

5 Fuel feeding hose, gasket and O-ring

Rotating shaft seal

Gasket for hydraulic equipment

Seal for fire wall

(v) Ship applications

10 Stern seal for screw propeller shaft

Suction and exhaust valve stem seals for diesel engine

Valve seal for butterfly valve

Stem seal for butterfly valve

(vi) Food and medicine applications

15 Seal for plate heat exchanger

Solenoid valve seal for vending machine

Plugs for chemicals

(vii) Electrical applications

Insulation oil cap for a train of the Shikansen line

20 Venting seal for liquid ring transmission

Jacket for oil well cable

Further the molded article of the present invention can be used for O-ring, sealing material, hose, tube, diaphragm, roll, lining and coating in equipment for producing semiconductor, liquid crystal panel, plasma display panel, plasma address liquid crystal panel, field emission display panel, substrate for solar battery, etc., for example, CVD equipment, etching equipment, oxidation/diffusion equipment,

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electrical equipment, sealing of an oven such as an electric oven, terminal treatment of sheath type heater, sealing of window frame of microwave oven, adhesion of CRT wedge and neck, adhesion of instrumentation parts of automotive, sealing of joints of kitchen, bath
5 room and lavatory, etc.

The present invention is then explained concretely by means of examples, but is not limited thereto.

PREPARATION EXAMPLE 1

10 A 3-liter autoclave equipped with a thermometer, stirrer, nitrogen gas feeding tube and pressure reducing device was charged with 1,500 ml of pure water and 2 g of ammonium perfluorooctanoate. After the inside of the autoclave was sufficiently replaced with a vinylidene fluoride/hexafluoropropylene/tetrafluoroethylene gas
15 mixture (hereinafter referred to as VdF/HFP/TFE, mole ratio: 18/71/11), a pressure and temperature of the inside of the autoclave were increased to 16 kg/cm²G and 80°C, respectively. Then 10 ml of a 0.3 % aqueous solution of ammonium persulfate was introduced under pressure with stirring. Since a pressure drop arose by the polymerization reaction,
20 when the inside pressure decreased to 15 kg/cm²G, a chain transfer agent I(CF₂)₄I (1.3g) was introduced under pressure. At the time when the inside pressure was further decreased to 14 kg/cm²G, it was again increased to 16 kg/cm²G with a VdF/HFP/TFE gas mixture (50/20/30 in mole ratio). Thereafter the polymerization was continued while
25 adjusting the inside pressure within the range of from 14 to 16 kg/cm²G in such a manner.

When a total pressure drop reached 5 kg/cm²G after starting

of the polymerization reaction, 1.8 g of $\text{CF}_2=\text{CFOCF}_2\text{CF}_2\text{CH}_2\text{I}$ was introduced. The polymerization was continued within the pressure range of from 14 to 16 $\text{kg/cm}^2\text{G}$ similarly. When a reduction of an amount of the gas mixture in a bomb reached 400 g, the inside pressure
5 was liberated to terminate the polymerization reaction. The obtained dispersion was frozen, coagulated and dried to obtain a polymer (hereinafter referred to as "Polymer A").

As a result of NMR analysis, components of the obtained polymer was $\text{VdF/HFP/TFE}=50/20/30$ % by mole. According to GPC
10 measurement, a number average molecular weight thereof was 140,000 (based on polystyrene). The iodine content thereof was 0.55 % by weight according to an elementary analysis.

PREPARATION EXAMPLE 2

15 A 3-liter autoclave equipped with a thermometer, stirrer, nitrogen gas feeding tube and pressure reducing device was charged with 1,500 ml of pure water and 1.5 g of ammonium perfluorooctanoate. After the inside of the autoclave was sufficiently replaced with a vinylidene fluoride/hexafluoropropylene gas mixture (hereinafter
20 referred to as VdF/HFP) (mole ratio: 45/55), a pressure and temperature of the inside of the autoclave were increased to 14 $\text{kg/cm}^2\text{G}$ and 80°C , respectively. Then 4.5 g of $\text{I}(\text{CF}_2\text{CF}_2)_2\text{I}$ as a polymerization initiator (25°C) was added and 10 ml of a 3 % aqueous solution of ammonium persulfate was introduced under pressure with stirring. Since a
25 pressure drop arose by the polymerization reaction, when the inside pressure decreased to 13 $\text{kg/cm}^2\text{G}$, the inside pressure was again increased to 15 $\text{kg/cm}^2\text{G}$ with a VdF/HFP gas mixture (78/22 in mole

ratio). Thereafter the polymerization was continued while adjusting the inside pressure within the range of from 13 to 15 kg/cm²G in such a manner. When a reduction of an amount of the gas mixture in a bomb reached 400 g, the inside pressure was liberated to terminate the polymerization reaction. The obtained dispersion was frozen, coagulated and dried to obtain a polymer (hereinafter referred to as "Polymer B").

As a result of NMR analysis, components of the obtained polymer was VdF/HFP=78/22 % by mole. According to GPC measurement, a number average molecular weight thereof was 41,000 (based on polystyrene). The iodine content thereof was 0.6 % by weight according to an elementary analysis.

PREPARATION EXAMPLE 3

A 1-liter separable flask equipped with a thermometer, stirrer, nitrogen gas feeding tube and pressure reducing device was charged with 400 g of pure water, 0.2 g of sodium bicarbonate, 1 g of sodium dodecylsulfate, 1 g of polyoxyethylene nonyl phenyl ether and 100 g of a monomer mixture (ethyl acrylate/2-iodoethyl acrylate = 99/1 % by weight). After the inside of the flask was sufficiently replaced with nitrogen gas, 0.01 g of sodium hydrosulfite, 0.002 g of sodium formaldehyde sulfoxylate and 0.005 g of t-butyl hydroperoxide were added to initiate a polymerization reaction at 35°C. After six-hour reaction had been carried out so that a conversion of the polymerization became not less than 99 %, the reaction product was subjected to salting-out, washing with water and drying to obtain a polymer (hereinafter referred to as "Polymer C").

The iodine content of the obtained polymer was 0.43 % by weight as a result of elementary analysis.

PREPARATION EXAMPLE 4

5 A 1-liter separable flask equipped with a thermometer, stirrer, nitrogen gas feeding tube and pressure reducing device was charged with 400 g of pure water, 0.2 g of sodium bicarbonate, 1 g of sodium dodecylsulfate, 1 g of polyoxyethylene nonyl phenyl ether and 100 g of a monomer (ethyl acrylate = 100 % by weight). After the inside of the
10 flask was sufficiently replaced with nitrogen gas, 0.01 g of sodium hydrosulfite, 0.002 g of sodium formaldehyde sulfoxylate and 0.005 g of t-butyl hydroperoxide were added to initiate a polymerization reaction at 35°C. After six-hour reaction had been carried out so that a conversion of the polymerization became not less than 99 %, the reaction product
15 was subjected to salting-out, washing with water and drying to obtain a polymer (hereinafter referred to as "Polymer D").

EXAMPLE 1

To 100 parts of Polymer A prepared in Preparation Example 1
20 were mixed 1.4 parts of 1-hydroxycyclohexyl phenylketone as a photoinitiator and 4.7 parts of trimethylolpropane triacrylate (TMPTA) as a polyfunctional unsaturated compound (crosslinking aid), and the mixture was kneaded and uniformly dispersed with an internal mixer. Then the obtained composition was subjected to pre-molding by
25 pressing at a specific temperature to obtain an about 0.5 mm thick sheet.

The sheet was passed through a conveyor type ultraviolet ray

irradiation equipment to be subjected to irradiation with ultraviolet rays. Thereby a crosslinked article was obtained. With respect to the irradiation conditions, an intensity of ultraviolet rays was about 165 mW/cm², an irradiation time was about 30 seconds and an ambient
5 temperature was room temperature (about 25°C).

With respect to the crosslinked article, solubility in acetone (the crosslinked article was dipped in acetone at room temperature for three hours with stirring, and solubility was observed with naked eyes) and physical properties in normal state according to JIS K-6301 were
10 measured. The results are shown in Table 1.

EXAMPLES 2 to 5

Components shown in Table 1 were mixed and pre-molded in the same manner as in Example 1 to obtain an about 0.5 mm thick sheet.
15 The sheet was subjected to ultraviolet ray irradiation under the same irradiation conditions as in Example 1 to obtain a crosslinked article and its solubility in acetone and physical properties in normal state were determined. The results are shown in Table 1.

TABLE 1

	Example				
	1	2	3	4	5
Polymer composition (part by weight)					
Polymer					
Polymer A	100	100	100	100	100
Polymer B					
Polymer C					
Photoinitiator					
1-hydroxycyclohexyl phenylketone	1.4	4.2			4.2
2,2-dimethoxy-2- phenylacetone			2.7		
Benzophenone				1.9	
Photoinitiating aid					
Triethanolamine				0.63	
Polyfunctional unsaturated compound					
TMPTA	4.7		4.7	4.7	4.7
TAIC		4			

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Physical properties of crosslinked article					
Solubility in acetone		Insoluble	Insoluble	Insoluble	Insoluble
Physical properties in normal state					
100 % tensile stress (MPa)		3	1	1	1
Strength at break (MPa)		6	4	3.5	4.5
Elongation at break (%)		700	540	520	550
Hardness (JIS A)		56	55	55	54

EXAMPLES 6 to 8

Components shown in Table 2 were mixed and pre-molded in the same manner as in Example 1 to obtain an about 0.5 mm thick sheet. In Examples 6 and 7, Polymer B prepared in Preparation Example 2 was
5 used as an iodine-containing polymer, and in Example 8, Polymer C prepared in Preparation Example 3 was used as an iodine-containing polymer.

The sheet was subjected to ultraviolet ray irradiation under the same irradiation conditions as in Example 1 to give a crosslinked
10 article and its solubility in acetone and physical properties in normal state were determined. The results are shown in Table 2.

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TABLE 2

	Example		
	6	7	8
Polymer composition (part by weight)			
Polymer			
Polymer A			
Polymer B	100	100	
Polymer C			100
Photoinitiator			
1-hydroxycyclohexyl phenylketone	4.2	4.2	2.1
2,2-dimethoxy-2- phenylacetone			
Benzophenone			
Photoinitiating aid			
Triethanolamine			
Polyfunctional unsaturated compound			
TMPTA			
TAIC	4	8	4

- continued

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Physical properties of
crosslinked article

Solubility in acetone	Insoluble	Insoluble	Insoluble
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Physical properties in
normal state

100 % tensile stress (MPa)	0.3	0.5	2
Strength at break (MPa)	2	5	4
Elongation at break (%)	900	370	450
Hardness (JIS A)	36	50	58

COMPARATIVE EXAMPLES 1 to 5

Components shown in Table 3 were mixed and pre-molded in the same manner as in Example 1 to obtain an about 0.5 mm thick sheet. In Comparative Examples 1 and 2, a fluorine-containing elastomer of VDF/HFP/TFE terpolymer (DAIEL G501 available from DAIKIN INDUSTRIES, LTD.) containing no iodine was used as a polymer, in Comparative Example 3, Polymer A prepared in Preparation Example 1 was used as a polymer (no photoinitiator was used), in Comparative Example 4, Polymer A was used as a polymer (no polyfunctional unsaturated compound was used), and in Comparative Example 5, Polymer D prepared in Preparation Example 4 and having neither iodine nor bromine was used as a polymer.

The sheet was subjected to ultraviolet ray irradiation under the same irradiation conditions as in Example 1 to obtain a crosslinked article and its solubility in acetone and physical properties in normal state were determined. The results are shown in Table 3.

TABLE 3

Polymer composition (part by weight)	Comparative Example				
	1	2	3	4	5
Polymer					
G501	100	100			
Polymer A			100	100	
Polymer D					100
Photoinitiator					
1-hydroxycyclohexyl phenylketone	2.1	2.1		2.1	2.1
2,2-dimethoxy-2- phenylacetone					
Benzophenone					
Photoinitiating aid					
Triethanolamine					
Polyfunctional unsaturated compound					
TMPTA	4.7				
TAIC		4	4	4	4

- continued -

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Physical properties of
crosslinked article

Solubility in acetone	Dissolved	Dissolved	Dissolved	Dissolved	Dissolved
Physical properties in normal state					
100 % tensile stress (MPa)	Plastic deformation	Plastic deformation	Plastic deformation	Plastic deformation	Plastic deformation
Strength at break (MPa)	Plastic deformation	Plastic deformation	Plastic deformation	Plastic deformation	Plastic deformation
Elongation at break (%)	Unmeasurable	Unmeasurable	Unmeasurable	Unmeasurable	Unmeasurable
Hardness (JIS A)	Unmeasurable	Unmeasurable	Unmeasurable	Unmeasurable	Unmeasurable

INDUSTRIAL APPLICABILITY

According to the present invention, by using iodine and/or bromine as a crosslinking point, it is possible to carry out crosslinking of various polymers including fluorine-containing polymers which have
5 been very difficult to crosslink with ultraviolet rays, and molding or processing can be made easily at working site at low temperature.

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